

Cite this: DOI: 10.1039/c1dt10991j

www.rsc.org/dalton

PAPER

**Magneto-structural studies of two new cobalt(II)-*N,N*-diisobutylicotinamide compounds:  $[\text{CoLCl}_2]_n$  and  $[\text{Co}(\text{L})_2(\text{H}_2\text{O})_4][\text{CoLBr}_3]_2 \cdot 2\text{H}_2\text{O}^\dagger$** Ajay Pal Singh Pannu,<sup>a</sup> Pratibha Kapoor,<sup>\*b</sup> Geeta Hundal,<sup>a</sup> Ramesh Kapoor,<sup>\*e</sup> Montserrat Corbella,<sup>\*c</sup> Núria Aliaga-Alcalde<sup>\*c,d</sup> and Maninder Singh Hundal<sup>\*a</sup>

Received 26th May 2011, Accepted 26th August 2011

DOI: 10.1039/c1dt10991j

Two similar synthetic pathways using the ligand *N,N*-diisobutylicotinamide (L) with anhydrous  $\text{CoX}_2$  salts (being  $\text{X} = \text{Cl}^-$ ,  $\text{Br}^-$ ) led to different species: a one-dimensional system,  $[\text{CoLCl}_2]_n$ , **1**, and an ionic product  $[\text{Co}(\text{L})_2(\text{H}_2\text{O})_4][\text{CoLBr}_3]_2 \cdot 2\text{H}_2\text{O}$ , **2**, respectively. Compound **1** is a polymer in which ligand L coordinates to tetrahedral  $\text{Co}^{\text{II}}$  ions in a bidentate bridging fashion using the pyridine nitrogen and carbonyl oxygen atoms. Compound **2** consists of one octahedral cationic  $[\text{Co}(\text{L})_2(\text{H}_2\text{O})_4]^{2+}$  entity and two tetrahedral anionic  $[\text{CoLBr}_3]^-$  units. In this system, the ligand molecules coordinate only through the pyridine nitrogen atoms. The magnetic properties of **1** and **2** were investigated in the temperature range of 2.0 to 300.0 K and correlations between both (due to the existence of similar features) examined. The study of the magnetic properties of **1** was carried out by considering each  $\text{Co}^{\text{II}}$  ion as a perfectly isolated system, hence,  $J = 0$ , but taking into account a significant zero-field splitting contribution due to distortions on the tetrahedral environment of the cobalt atoms. The fit of the magnetic susceptibility data together with reduced magnetization *vs*  $H/T$  measurements provided similar parameters ( $|D| = 10.8 \text{ cm}^{-1}$ ,  $g_{\perp} = 1.92$ ,  $g_{\parallel} = 2.92$  for the former and  $|D| = 11.04 \text{ cm}^{-1}$  and  $g = 2.05$  for the latter, respectively). On the other hand, the magnetic response of compound **2** has been analyzed using a model which considers the presence of two tetrahedral and one octahedral  $\text{Co}(\text{II})$  ions ( $\text{Co}_{\text{Td}}$  and  $\text{Co}_{\text{Oh}}$ ). The study was carried out in two separated blocks, above and below 80 K, where only the most significant effects at each interval of temperature were considered. As a result, the analysis of the magnetic data shows weak antiferromagnetic interactions between the  $\text{Co}_{\text{Oh}}$  and the two  $\text{Co}_{\text{Td}}$  ions ( $J = -0.41 \text{ cm}^{-1}$ ) in **2**. The best fit parameters were  $g_{\text{Co}_{\text{Td}}} = 2.89$ ,  $g_{\text{Co}_{\text{Oh}}} = 3.50$ ,  $|D_{\text{Co}_{\text{Td}}}| = 10.62 \text{ cm}^{-1}$ ,  $|E_{\text{Co}_{\text{Td}}}| = 2.95 \text{ cm}^{-1}$ ,  $\Delta = 240.9 \text{ cm}^{-1}$  and  $J_{\text{L.S}} = -107.1 \text{ cm}^{-1}$ , from where  $\lambda$  was calculated with a final value of  $-144.8 \text{ cm}^{-1}$  ( $J_{\text{L.S}} = A\kappa\lambda$ ). The approximations performed to obtain these values provide reasonable results in agreement with compound **1** and also to other systems in the literature.

**1. Introduction**

Magnetic studies of  $\text{Co}(\text{II})$  complexes have gained impetus with the growing branch of magnetic metal-organic frameworks

<sup>a</sup>Department of Chemistry, Guru Nanak Dev University, Amritsar, 143005, India. E-mail: hundal\_chem@yahoo.com

<sup>b</sup>Department of Chemistry, Panjab University, Chandigarh, 160014, India. E-mail: pkapoor@pu.ac.in

<sup>c</sup>Departament de Química Inorgànica, Universitat de Barcelona (UB), Martí i Franquès 1-11, 08028, Barcelona, Spain. E-mail: montse.corbella@qi.ub.es

<sup>d</sup>ICREA Junior Researcher at the UB (ICREA: Institució Catalana de Recerca i Estudis Avançats), 08010, Barcelona, Spain. E-mail: nuria.aliaga@qi.ub.es

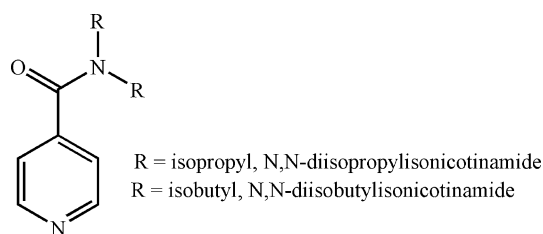
<sup>e</sup>Department of Chemistry, Indian Institute of Science Education and Research, Mohali, Chandigarh, 160 019, India. E-mail: rkapoor@iisermohali.ac.in

<sup>†</sup> Electronic supplementary information (ESI) available: CCDC reference numbers 808174–808175. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c1dt10991j

(MMOF).<sup>1</sup> As put forth by M. Kurmoo<sup>2</sup> the choice of  $\text{Co}(\text{II})$  for this purpose is based upon its available range of geometries,<sup>3</sup> commonly occurring high spin ( $S = 3/2$ ) state, easy identification of different (magnetic) phases by color variation<sup>4</sup> and the highest Curie temperature and magnetic anisotropy among the three ferromagnets of the first row transition elements. Magnetism is a cooperative phenomenon therefore magnetic exchange between various metal centres in polynuclear compounds is essential for the realization of any such effect substantially. At the same time the generation of MOF usually follows an order of structural condensation progressing from 1D chains to 2D layers finally giving 3D networks. Therefore it is very important to model and understand the systems of low complexity first and then gradually proceed from there to tackle the complicated 3D systems. The magnetic response of  $\text{Co}(\text{II})$  is tuned by the coordination number and environment, therefore a number of compounds combining both, tetrahedral and octahedral  $\text{Co}(\text{II})$  atoms have been

crystallographically characterized and few researchers such as Cano *et al.*<sup>5</sup> and Liang *et al.*<sup>6</sup> have been able to elucidate the magnetic behavior of such complex systems. Following their steps we have recently studied a Co<sub>3</sub> system and discussed its magnetic properties.<sup>7</sup>

From a synthetic point of view, it is well known that among various pyridine based ligands, nicotinic acid derivatives such as isonicotinic acid, isonicotinamide and nicotinamide are employed for bringing various metal centers in close vicinity through hydrogen bonding or coordination polymerization or using a combination of both.<sup>8–16</sup> Therefore, we have extended our previous family of compounds based on the coordination of *N,N,N',N'*-tetraalkylpyridine-2,6-dicarboxamide derivatives with first row transition metals<sup>17</sup> to *N,N*-dialkylisonicotinamides systems (Scheme 1) containing Co(II) centers,<sup>7</sup> hoping that this would result in the formation of such 2D/3D networks with Co(II) ions in close proximity. Here, we present the synthesis, structure and magnetic properties of two new compounds: [Co(LCl<sub>2</sub>)<sub>n</sub>], **1**, and [Co(L)<sub>2</sub>(H<sub>2</sub>O)<sub>4</sub>][Co(LBr<sub>3</sub>)<sub>2</sub>·2H<sub>2</sub>O], **2**, where L is *N,N*-diisobutylisonicotinamide.



**Scheme 1** *N,N*-dialkylisonicotinamide ligands.

In our previous communication,<sup>7</sup> the fully substituted *N,N*-diisopropylisonicotinamide derivative lead to the creation of a rare 1D coordination polymer [Co<sub>3</sub>L'<sub>4</sub>Cl<sub>6</sub>] containing Co<sup>II</sup><sub>Td</sub>–Co<sup>II</sup><sub>Oh</sub>–Co<sup>II</sup><sub>Td</sub> trinuclear units (L' = *N,N*-diisopropylisonicotinamide). A similar trinuclear arrangement of Co<sup>II</sup> ions was achieved for compound **2**, through intermolecular hydrogen bonding involving non-coordinated water molecules and this prompted the magnetic study of this system. The results have been compared with magnetic data obtained for compound **1** which is also a 1D coordination polymer.

## 2. Experimental

All additions and manipulations were carried out under a dry nitrogen environment unless otherwise stated. All solvents were distilled prior to use (benzene, toluene over P<sub>4</sub>O<sub>10</sub> and acetonitrile from calcium hydride). Anhydrous cobalt(II) chloride was prepared by treating a powdered sample of hydrated CoCl<sub>2</sub> with thionyl chloride and refluxing the contents for a few hours till evolution of SO<sub>2</sub> ceased. The anhydrous product was washed with petroleum ether and dried *in vacuo*. CoBr<sub>2</sub> was prepared *in situ* by reacting anhydrous CoCl<sub>2</sub> (1.3 g, 10 mmol) with two moles of anhydrous KBr (2.38 g, 10 mmol) in about 60 mL of CH<sub>3</sub>CN. The contents were stirred for about 8 h and the precipitated KCl was removed by filtration under vacuum. The filtrate was used for further reaction with the ligand. Elemental analyses (C, H, N) were performed with a Perkin–Elmer model 2400 CHN analyzer. IR spectra were recorded using KBr pellets with a Perkin–Elmer RX-1

FTIR spectrophotometer. Thermal analyses was carried out with a Shimadzu-DTG 60 analyser. <sup>1</sup>H NMR spectra of the ligands were recorded with a 300 MHz JEOL FT NMR spectrometer with TMS as the reference compound. UV-vis spectra were recorded with a Shimadzu Pharmaspec UV-1700 UV-vis spectrophotometer. Molar conductance of millimolar solutions of the compounds were measured with a conductivity bridge-Digital Conductivity Meter CC 601. Magnetic susceptibility measurements between 2–300 K and magnetization measurements, at 2 K, between 0–5 T, were carried out with a SQUID magnetometer Quantum Design Magnetometer, model MPMP at the “Unitat de Mesures Magnètiques (Universitat de Barcelona)” using polycrystalline samples of compounds **1** and **2**, respectively. Two different magnetic fields were used for the susceptibility measurements, 0.3 T (2–30 K) and 0.5 T (2–300 K), with superimposable graphs. The diamagnetic corrections were evaluated from Pascal's constants. *R* is the agreement factor defined as  $\Sigma[(\chi_M T)^{\text{calcd}} - (\chi_M T)^{\text{exptl}}]^2 / \Sigma[(\chi_M T)^{\text{exptl}}]^2$ .

***N,N*-diisobutylisonicotinamide (L).** The ligand L was prepared as per the method reported earlier for ligand *N,N*-diisopropylisonicotinamide.<sup>7</sup> Isonicotinic acid (0.15 mol) was reacted with thionyl chloride to obtain isonicotinyl chloride hydrochloride. It was added to a mixture of about 100 mL toluene, 0.30 mol of pyridine and diisobutylamine (0.46 mol). The mixture was refluxed for 15–20 min and then kept at room temperature overnight. The solid obtained on cooling was removed by filtration and the filtrate was treated with 50% aqueous NaOH solution and chilled. The toluene layer was separated and the alkaline solution was extracted with ether. The combined toluene and ether layers were dried over sodium sulphate and excess solvent was removed by distillation. The yellow colored distillate solidified on cooling. The final product was obtained after recrystallization from *n*-heptanes. Color: yellowish-brown. Anal. found: C, 71.67; H, 9.24; N, 11.82%. Calc. for C<sub>14</sub>H<sub>22</sub>N<sub>2</sub>O: C, 71.79; H, 9.40; N, 11.97%. M.p., 54–56 °C. IR:  $\nu_{\text{CO}} = 1632 \text{ cm}^{-1}$ . <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  (0.69; d, 6H, CH<sub>3</sub>, *J* = 6.3 Hz);  $\delta$  (0.92; d, 6H, CH<sub>3</sub>, *J* = 6.6 Hz);  $\delta$  (1.78; m, 1H, CH);  $\delta$  (2.08; m, 1H, CH);  $\delta$  (2.94; d, 2H, CH<sub>2</sub>, *J* = 7.5 Hz);  $\delta$  (3.28; d, 2H, CH<sub>2</sub>, *J* = 7.5 Hz);  $\delta$  (7.17; dd, 2H, Py, *J* = 12, *J* = 13.8);  $\delta$  (8.59; d, 2H, Py, *J* = 3.9).

**[Co(LCl<sub>2</sub>)<sub>n</sub>] (1).** This compound was prepared from a reaction mixture containing equimolar amounts of anhydrous CoCl<sub>2</sub> (2.58 g, 20 mmol) and L (4.68 g, 20 mmol) dissolved in about 25 mL of isobutylalcohol. The contents were stirred for 3–4 h which on keeping for 2–3 days at room temperature yielded a blue crystalline solid which was filtered and dried *in vacuo*. Anal. found: C, 46.03; H, 6.23; N, 7.40. Calc. for C<sub>14</sub>H<sub>22</sub>Cl<sub>2</sub>CoN<sub>2</sub>O: C, 46.13; H, 6.04 N, 7.69%. M.p.: 287–290 °C (d). Molar conductance ( $\Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$ ): 11.0 (CH<sub>3</sub>CN). IR:  $\nu_{\text{CO}} 1582 \text{ cm}^{-1}$ .

**[Co(L)<sub>2</sub>(H<sub>2</sub>O)<sub>4</sub>][Co(LBr<sub>3</sub>)<sub>2</sub>·2H<sub>2</sub>O] (2).** To the blue solution of CoBr<sub>2</sub> (2.187 g, 10 mmol) in acetonitrile ligand L (2.34 g, 10 mmol) was added in a minimum amount of isobutylalcohol. The contents were stirred for a few hours at room temperature. An intense blue solid separated out of the reaction mixture after about 24 h, which was filtered and dried *in vacuo*. Anal. found: C, 39.32; H, 6.02; N, 6.46. Calc. for C<sub>56</sub>H<sub>100</sub>Br<sub>6</sub>Co<sub>3</sub>N<sub>8</sub>O<sub>10</sub>: C, 39.49; H, 5.88; N, 6.58%. M.p.: 293 °C (d). Molar conductance ( $\Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$ ): 233 (CH<sub>3</sub>CN). IR:  $\nu_{\text{CO}} 1606 \text{ cm}^{-1}$ .

## X-ray data collection

The crystals for X-ray diffraction studies on compounds **1** and **2** were grown by slow evaporation from their respective saturated solutions in isopropyl alcohol. Data collection for compound **1** was carried out with a Nonius kappa CCD2000 with a graded mirror, using Cu-K $\alpha$  radiation ( $\lambda = 1.5418 \text{ \AA}$ ) at 120 (2) K whereas that for compound **2** was carried out with an Oxford Diffraction Gemini diffractometer equipped using a Mo-K $\alpha$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ) source at 150(2) K. The data were corrected for Lorentz and polarization factors as well as absorption. The structures of both the compounds **1** and **2** were solved by direct methods using SIR97<sup>18a</sup> and refined on  $F^2$  using SHELX-97.<sup>18b</sup> All non-hydrogen atoms were refined using anisotropic thermal parameters. The hydrogen atoms were included in the ideal positions with fixed isotropic  $U$  value and were riding on their respective non-hydrogen atoms. Compound **1** was solved in the non-centrosymmetric space group  $P2_1$  with one restraint over the floating point origin. The Flack parameter (0.015(7)) indicates that it is in the correct absolute configuration. A refinement of 181 parameters gave a final  $R$  0.0400,  $wR$  0.0986 for all 1771 reflections and  $R$  0.0396,  $wR$  0.0985 for 1751 observed [ $I > 2\sigma(I)$ ] reflections].

Compound **2** was solved in the triclinic space group  $P\bar{1}$  successfully with all the non-hydrogen atoms being anisotropically refined. Hydrogens of four coordinated and two lattice water molecules could not be located with sensible geometries from the difference Fourier maps hence the final model is devoid of twelve hydrogen atoms per molecule. The converged model shows unusual residual peaks of electron density  $4.6 \text{ e \AA}^{-3}$  and less very close to the heavy atoms which are not due to disorder or solvent but probably due to non-merohedral twinning as explained in the cif, resulting in A level errors. The final residual index obtained refining 376 parameters is  $R$  0.1057,  $wR$  0.3458 for 7521 observed reflections [ $I > 2\sigma(I)$ ] and  $R$  0.1531  $wR$  0.3706 for all 12016 reflections. Experimental details of the X-ray analyses of compounds **1** and **2** are provided in Table 1 while selected bond distances and angles for both these compounds are listed in Table 2.

## Results and discussion

The coordination behavior of **L** is expected to resemble that of the corresponding diisopropyl derivative.<sup>7</sup> The enhanced structural rigidity in these isonicotinamide derivatives favors the bidentate bridging mode of coordination between metal centers and the same is observed in compound **1** whereas the ligand coordinates in a monodentate fashion using only its pyridine nitrogen atom in compound **2**. The reactions of **L** with  $\text{CoCl}_2$  and  $\text{CoBr}_2$  yielded: (i) a polymeric solid compound containing tetrahedral  $\text{Co}^{\text{II}}$  units,  $[\text{CoLCl}_2]_n$ , **1** and (ii) an ionic product  $[\text{Co}(\text{L})_2(\text{H}_2\text{O})_4][\text{CoLBr}_3]_2 \cdot 2\text{H}_2\text{O}$ , **2**, respectively. The nature of these products is also reflected in their conductivity data. The  $\nu_{\text{C=O}}$  is observed as a strong band at  $1582 \text{ cm}^{-1}$  in compound **1** as compared to  $1632 \text{ cm}^{-1}$  in the free ligand, showing a significant shift to a lower wave number due to coordination of the carboxamide oxygen to the metal center.

The absorption spectra for compound **1** and **2** are given in Fig. 1. Generally, for  $\text{Co}^{\text{II}}$  tetrahedral and pseudotetrahedral species, three transitions,  ${}^4\text{T}_1 \leftarrow {}^4\text{A}_2$  ( $\nu_1$ ),  ${}^4\text{T}_1(\text{F}) \leftarrow {}^4\text{A}_2(\nu_2)$  and  ${}^4\text{T}_1(\text{P}) \leftarrow {}^4\text{A}_2(\nu_3)$  may be observed although  $\nu_1$  usually lies at low

**Table 1** Crystal data and structure refinement for **1** and **2**

	<b>1</b>	<b>2</b>
Empirical formula	$\text{C}_{14}\text{H}_{22}\text{Cl}_2\text{CoN}_2\text{O}$	$\text{C}_{56}\text{H}_{100}\text{Br}_6\text{Co}_3\text{N}_8\text{O}_{10}$
Formula weight	364.17	1701.68
$T/\text{K}$	120(2)	150(2)
Wavelength/ $\text{\AA}$	1.54178	0.71073
Space group	Monoclinic, $P2_1$	Triclinic, $P\bar{1}$
$a/\text{\AA}$	9.3915(4)	9.8031(3)
$b/\text{\AA}$	7.3850(3)	11.8076(5)
$c/\text{\AA}$	13.1072(4)	15.7629(7)
$\alpha/^\circ$	90	92.503(4)
$\beta/^\circ$	109.658(2)	91.003(3)
$\gamma/^\circ$	90	91.025(3)
Volume/ $\text{\AA}^3$	856.08(6)	1822.23(12)
$D_c/\text{Mg m}^{-3}$	1.413	1.551
$\mu/\text{mm}^{-1}$	10.701	4.018
$F(000)$	378	863
Reflections collected/unique	3327/1771	23039/12016
	[ $R(\text{int}) = 0.0251$ ]	[ $R(\text{int}) = 0.0420$ ]
Data/restraints/parameters	1771/1/181	12016/0/376
Goodness-of-fit on $F^2$	1.262	1.332
Final $R$ indices [ $I > 2\sigma(I)$ ]	$R_1 = 0.0396$ $wR_2 = 0.0985$	$R_1 = 0.1057$ $wR_2 = 0.3458$
$R$ indices (all data)	$R_1 = 0.0400$ $wR_2 = 0.0986$	$R_1 = 0.1531$ $wR_2 = 0.3707$
CCDC No.	808174	808175

**Table 2** Selected bond lengths ( $\text{\AA}$ ) and angles ( $^\circ$ ) for **1** and **2**

<b>1</b>			
$\text{N}(1)\text{--Co}(1)^{\text{i}}$	2.052(5)	$\text{O}(1)\text{--Co}(1)\text{--N}(1)^{\text{ii}}$	92.02(18)
$\text{O}(1)\text{--Co}(1)$	1.989(4)	$\text{O}(1)\text{--Co}(1)\text{--Cl}(1)$	106.74(11)
$\text{Cl}(1)\text{--Co}(1)$	2.217(2)	$\text{N}(1)^{\text{iii}}\text{--Co}(1)\text{--Cl}(1)$	111.19(13)
$\text{Cl}(2)\text{--Co}(1)$	2.222(1)	$\text{O}(1)\text{--Co}(1)\text{--Cl}(2)$	114.41(11)
$\text{Co}(1)\text{--N}(1)^{\text{ii}}$	2.052(5)	$\text{N}(1)^{\text{iii}}\text{--Co}(1)\text{--Cl}(2)$	107.56(13)
		$\text{Cl}(1)\text{--Co}(1)\text{--Cl}(2)$	121.11(6)
<b>2</b>			
$\text{Br}(1)\text{--Co}(1)$	2.318(1)	$\text{N}(1)\text{--Co}(1)\text{--Br}(3)$	108.63(15)
$\text{Br}(2)\text{--Co}(1)$	2.370(1)	$\text{N}(1)\text{--Co}(1)\text{--Br}(1)$	106.82(16)
$\text{Br}(3)\text{--Co}(1)$	2.294(1)	$\text{Br}(3)\text{--Co}(1)\text{--Br}(1)$	112.87(6)
$\text{O}(3)\text{--Co}(2)$	2.082(5)	$\text{N}(1)\text{--Co}(1)\text{--Br}(2)$	101.49(16)
$\text{O}(4)\text{--Co}(2)$	2.112(5)	$\text{Br}(1)\text{--Co}(1)\text{--Br}(2)$	113.01(5)
$\text{Co}(1)\text{--N}(1)$	2.061(6)	$\text{O}(3)\text{--Co}(2)\text{--O}(4)^{\text{iii}}$	88.9(2)
$\text{Co}(2)\text{--O}(3)^{\text{iii}}$	2.082(5)	$\text{O}(3)^{\text{iii}}\text{--Co}(2)\text{--O}(4)^{\text{iii}}$	91.1(2)
$\text{Co}(2)\text{--O}(4)^{\text{iii}}$	2.112(5)	$\text{O}(3)^{\text{iii}}\text{--Co}(2)\text{--N}(3)^{\text{iii}}$	90.4(2)
$\text{Co}(2)\text{--N}(3)^{\text{iii}}$	2.134(5)	$\text{O}(4)\text{--Co}(2)\text{--N}(3)$	90.2(2)
$\text{Co}(2)\text{--N}(3)$	2.134(5)	$\text{O}(3)\text{--Co}(2)\text{--N}(3)^{\text{iii}}$	89.6(2)

$\text{i} = x, y + 1, z$ ;  $\text{ii} = x, y - 1, z$ ;  $\text{iii} = -x + 1, -y + 1, -z$ .

energy ( $2500\text{--}6000 \text{ cm}^{-1}$ ).<sup>4,19a-g</sup> The  ${}^4\text{T}_1(\text{F}) \leftarrow {}^4\text{A}_2(\nu_2)$  and  ${}^4\text{T}_1(\text{P}) \leftarrow {}^4\text{A}_2(\nu_3)$  transitions appear as multiple absorption bands in the near infra-red and visible regions, respectively. Therefore, in the regular tetrahedral and near-tetrahedral  $\text{Co}^{\text{II}}$  compounds only one d-d transition  ${}^4\text{T}_1(\text{P}) \leftarrow {}^4\text{A}_2$ , assigned as  $\nu_3$  is observed in the visible region. Compound **1**,  $[\text{CoLCl}_2]_n$  shows a closely spaced multiple structured band in the visible region with maxima at  $668 \text{ nm}$  ( $14,970 \text{ cm}^{-1}$ ,  $\epsilon = 430 \text{ l mol}^{-1}\text{cm}^{-1}$ ),  $624 \text{ nm}$  ( $16,025 \text{ cm}^{-1}$ ,  $\epsilon = 327 \text{ l mol}^{-1}\text{cm}^{-1}$ ) and at  $593 \text{ nm}$  ( $16,863 \text{ cm}^{-1}$ ,  $\epsilon = 352 \text{ l mol}^{-1}\text{cm}^{-1}$ ) ( $\text{CoNOCl}_2$  chromophore). In addition to this, very intense transitions are observed in the UV region  $250\text{--}255 \text{ nm}$  ( $\epsilon$  of the order of  $16760 \text{ l mol}^{-1}\text{cm}^{-1}$ ). The intensity of these transitions is consistent with being intraligand transition(s) or/and ligand

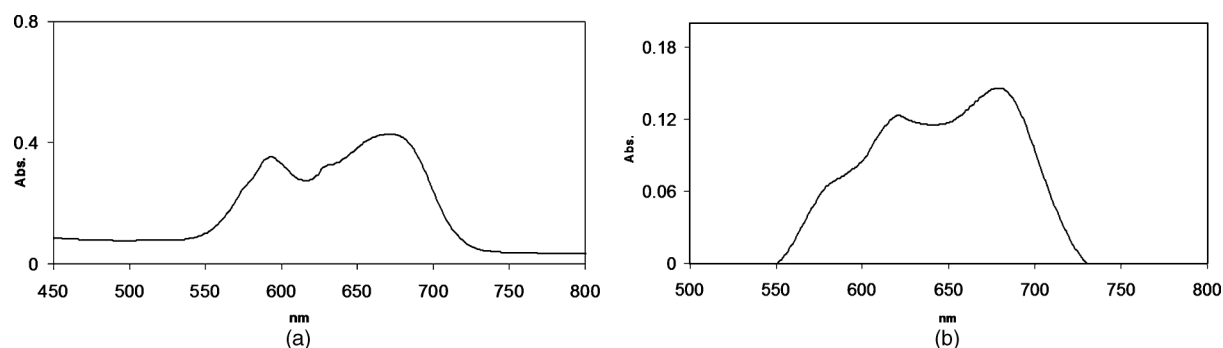


Fig. 1 Showing the absorption spectrum for (a) compound 1 (b) compound 2.

to metal charge-transfer transition(s). Similarly for compound **2**, a multiple structured band corresponding to  ${}^4T_1(P) \leftarrow {}^4A_2$  d-d transition (CoNBr<sub>3</sub> chromophore) is observed at 677 nm (14,771 cm<sup>-1</sup>,  $\epsilon = 145$  l mol<sup>-1</sup>cm<sup>-1</sup>) with a sharp shoulder at 620 nm (16129 cm<sup>-1</sup>,  $\epsilon = 134$  l mol<sup>-1</sup>cm<sup>-1</sup>) in the visible region. This splitting of the d-d band observed in the visible region corresponding to tetrahedral chromophores in compounds **1** and **2** is considered to originate from the reduction of the orbital degeneracy due to the difference in the ligand field strength of neutral ligand L and the halide donor atoms.<sup>19h-k</sup>

#### X-ray crystal structure analyses

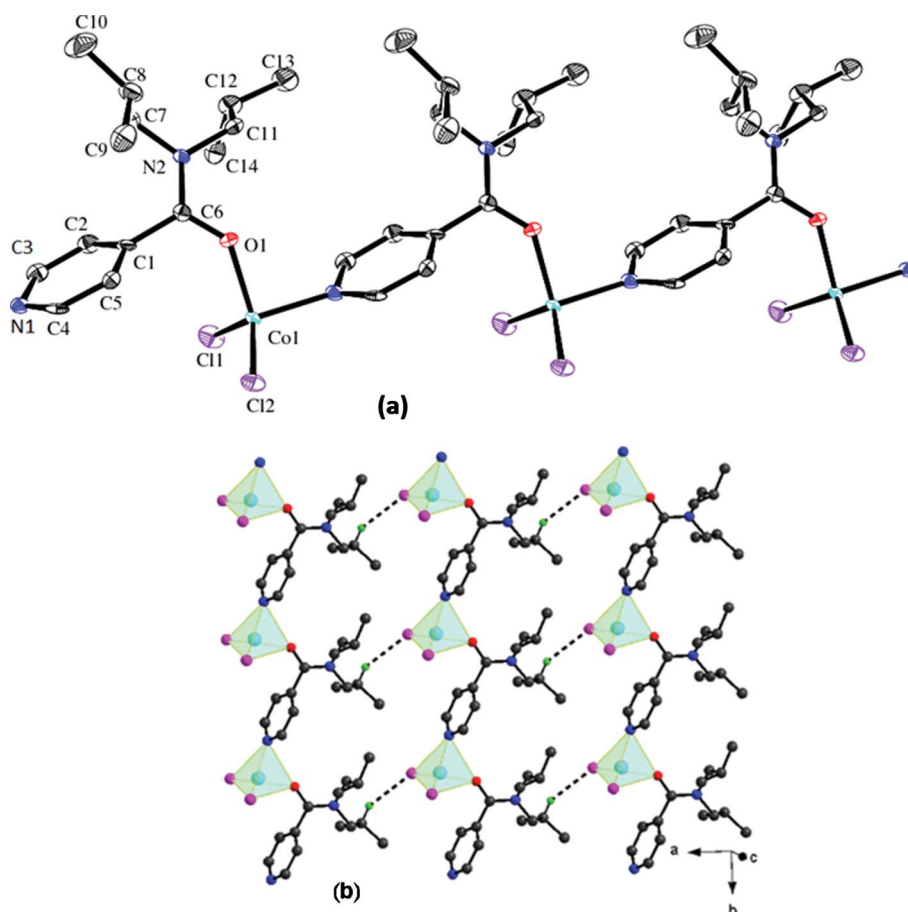
**Molecular and crystal structure of compound 1.** The ORTEP diagram of the asymmetric unit for complex **1** is shown in Fig. 2a along with the atom numbering scheme. The compound [CoLCl<sub>2</sub>]<sub>n</sub>, **1** is a 1D (one dimensional) coordination polymer in which every Co(II) centre occupies a tetrahedral geometry (CoNOCl<sub>2</sub> chromophore). The ligand L acts in a bridging bidentate fashion between metal centres, coordinating through the pyridine nitrogen and carbonyl oxygen atoms to form a 1D polymeric chain running along the *b* axis. The remaining two vacancies around every metal centre are filled by two chlorides Cl1 and Cl2 ions thus completing a tetrahedral geometry around the Co(II) ion. The Co1–O1, Co1–N1, Co1–Cl1 and Co1–Cl2 distances are 1.989(4) Å, 2.052(5) Å, 2.217(2) Å and 2.222(1) Å respectively. In our previous paper,<sup>7</sup> we reported a 1D coordination polymer containing trinuclear [Co<sub>3</sub>L<sub>4</sub>Cl<sub>6</sub>] units with mixed Co<sup>II</sup><sub>Td</sub>–Co<sup>II</sup><sub>Oh</sub>–Co<sup>II</sup><sub>Td</sub> geometries prepared by reaction of CoCl<sub>2</sub> with the ligand *N,N*-diisopropylisonicotinamide. In the present work, a similar reaction of CoCl<sub>2</sub> with *N,N*-diisobutylisonicotinamide yielded a 1D coordination polymer but no polynuclear entities are formed. This may probably be attributed to the increased steric bulk in *N,N*-diisobutylisonicotinamide preventing metal centers from coming into close proximity and forming polynuclear entities.

The crystal structure of compound **1** shows that the parallel 1D coordination chains are held together by C8–H8...Cl2<sup>i</sup> (3.718(7) Å, 2.86 Å, 147°) and C11–H11B...Cl2<sup>i</sup> (3.835(5) Å, 2.92 Å, 159) (where  $i = x - 1, +y, +z$ ) intermolecular hydrogen bonding interactions leading to the formation of a 2D sheet parallel to the *ab* plane (Fig. 2b). A third dimension is added to this system when these 2D sheets are cross linked by C2–H2...Cl1<sup>ii</sup> (3.496(6) Å, 2.75 Å, 138°) ( $ii = -x + 1, +y - 1/2, -z + 1$ ) and C4–H4...Cl2<sup>iii</sup> (3.542(6) Å, 2.89 Å, 128°) ( $iii = -x + 1, +y + 1/2, -z$ ) intermolecular H-bonds (Fig. S4, ESI†). Similar 2D sheets have been reported for

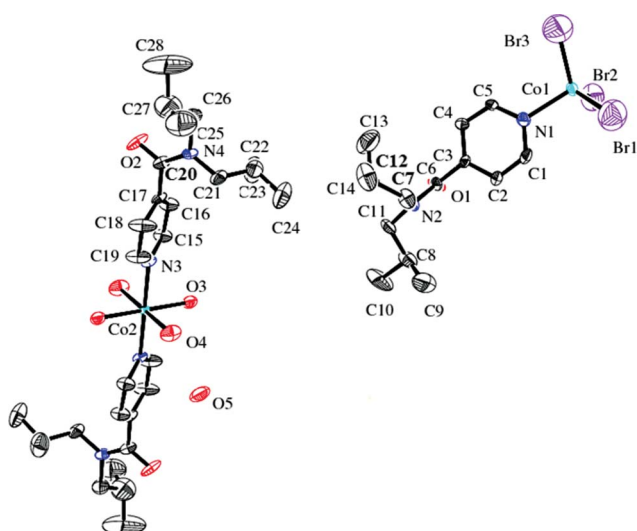
compound [Cu<sub>2</sub>(ClCH<sub>2</sub>CO<sub>2</sub>)<sub>4</sub>(L)]<sub>n</sub>, where –[Cu<sub>2</sub>(ClCH<sub>2</sub>CO<sub>2</sub>)<sub>4</sub>–L–Cu<sub>2</sub>(ClCH<sub>2</sub>CO<sub>2</sub>)<sub>4</sub>–] 1D coordination chains are held together by intermolecular H-bonding (L = *N,N*-diethylnicotinamide)<sup>15a</sup> with ligands themselves being the source of the hydrogen bonding functionalities. Nangia *et al.* also reported a similar sheet structure for compound [Ag(C<sub>5</sub>H<sub>4</sub>NCONH<sub>2</sub>)<sub>2</sub>]<sub>n</sub>[BF<sub>4</sub>]<sub>n</sub> having linear tapes of (pyridyl)N–Ag–O(amide) coordinated chains connected *via* N–H...F hydrogen bonds.<sup>16a</sup> Fowler and coworkers used combinations of coordination polymers and H-bonding to increase dimensionality in the case of Ag(I) compounds of pyridyl-derivatized ureas and oxalamides.<sup>20</sup>

**Molecular and crystal structure of compound 2.** The ORTEP diagram of complex **2** along with the atom numbering scheme is shown in Fig. 3. Compound **2** consists of discrete [Co(L)<sub>2</sub>(H<sub>2</sub>O)<sub>4</sub>]<sup>2+</sup> cations, [Co(L)Br<sub>3</sub>]<sup>-</sup> anions along with two non-coordinating water molecules and has the molecular composition [Co(L)<sub>2</sub>(H<sub>2</sub>O)<sub>4</sub>][Co(L)Br<sub>3</sub>]<sub>2</sub>·2H<sub>2</sub>O. In the [Co(L)<sub>2</sub>(H<sub>2</sub>O)<sub>4</sub>]<sup>2+</sup> structural unit, the Co<sup>II</sup> ion which rides on a crystallographic inversion center occupies an octahedral geometry (CoN<sub>2</sub>O<sub>4</sub> chromophore). It is coordinated by four water molecules defining the basal plane and by two ligand molecules both coordinating in a unidentate fashion through the ring nitrogen atoms which occupy the two *trans* positions in the octahedron. The orientation of the amide groups of both the coordinating ligand molecules is *trans* with respect to each other. The Co–N<sub>pyd</sub> distance is 2.134(5) Å while the Co–O<sub>water</sub> distances lies between 2.082(5)–2.112(5) Å. The anionic unit [CoLBr<sub>3</sub>]<sup>-</sup> has Co<sup>II</sup> centres occupying tetrahedral geometry. The ligand L coordinates to the metal centre in a monodentate fashion using its pyridine nitrogen atom with the Co–N<sub>pyd</sub> distance being 2.061(6) Å while the other three positions in the tetrahedron are occupied by three bromide atoms with Co–Br1, Co–Br2 and Co–Br3 distances being 2.318(1) Å, 2.370(1) Å and 2.294(1) Å, respectively.

The O5...Br1<sup>i</sup> (3.273(6) Å,  $i = -x + 1, -y, -z + 2$ ), O5...Br3<sup>ii</sup> (3.216(6) Å) and O5...O4<sup>ii</sup> (2.704(4) Å ( $ii = x - 1, +y, +z + 1$ )) hydrogen bonding interactions among both types of ionic structural units and non-coordinated water molecules leads to the formation of a 1D chain running diagonal to the *ab* plane in the crystal lattice (Fig. 4(a)). In this chain, every octahedral [Co(L)<sub>2</sub>(H<sub>2</sub>O)<sub>4</sub>]<sup>2+</sup> cationic unit is surrounded by two tetrahedral [CoLBr<sub>3</sub>]<sup>-</sup> anions to form a H-bonded trinuclear Co<sup>II</sup><sub>Td</sub>...Co<sup>II</sup><sub>Oh</sub>...Co<sup>II</sup><sub>Td</sub> unit (also involving uncoordinated water molecules) thereby maintaining overall charge neutrality in the compound. Such parallel chains are further held together by C27–H27B...Br2<sup>iii</sup> (3.841(11) Å, 2.93



**Fig. 2** (a) ORTEP diagram for (1) showing three units of the coordination polymer (b) 2D sheet formed by the combined effect of coordination bonding (along *b* axis) and intermolecular H-bonding (along *a* axis).



**Fig. 3** The ORTEP diagram of **2** along with the atom numbering scheme. To maintain the charge neutrality in the complex there are two centrosymmetric tetrahedral units  $[\text{Co}(\text{L}')\text{Br}_3]$  per octahedral  $[\text{Co}(\text{L}'')_2(\text{H}_2\text{O})_6]^{2+}$  unit. Only one of them is shown in this figure. Hydrogen atoms and one centrosymmetric lattice water (O5) have been removed for clarity.

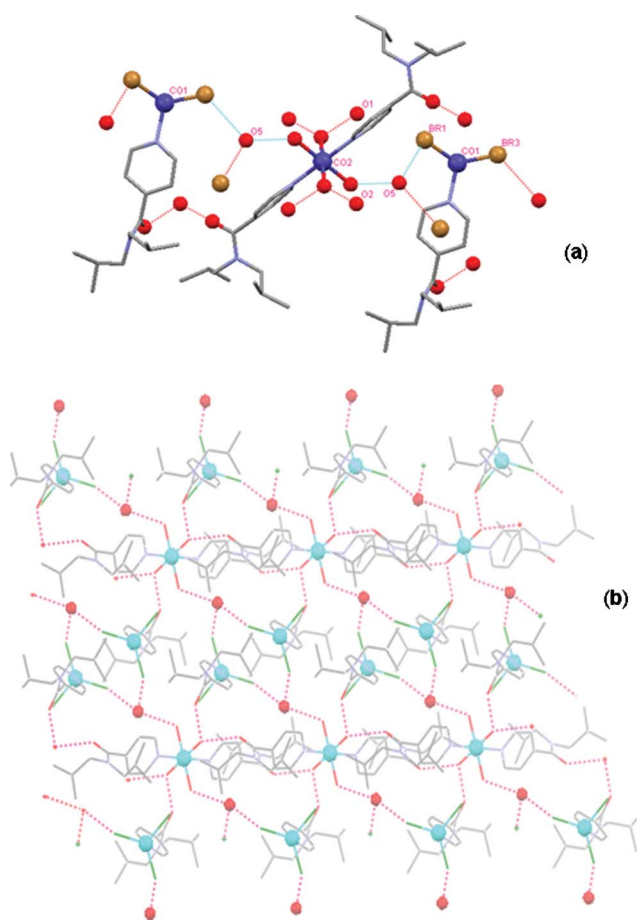
$\text{\AA}$ ,  $159^\circ$ , where  $iii = x - 1, +y, +z - 1$ ) into a 2D sheet extending along the *ab* plane (Fig. 4(b)).

### Magnetic studies

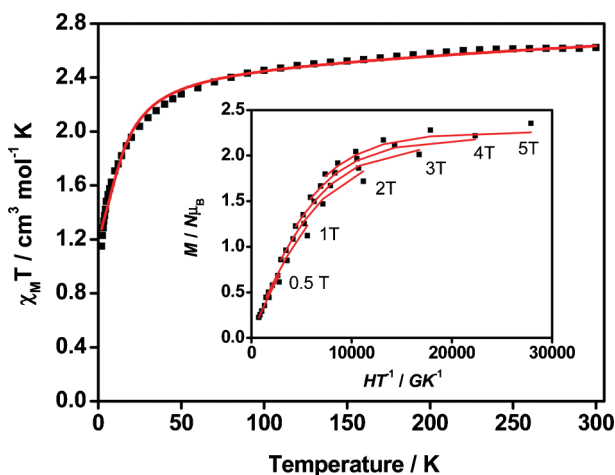
Variable-temperature magnetic susceptibility measurements were performed on a powdered polycrystalline sample of compound **1** with a 0.5 T applied field in the 2–300 K range. Fig. 5 shows a plot of  $\chi_M T$  vs  $T$  for this compound. The value of  $\chi_M T$  gradually decreases from  $2.62 \text{ cm}^3 \text{ mol}^{-1} \text{ K}$  at 300 K to  $2.27 \text{ cm}^3 \text{ mol}^{-1} \text{ K}$  at 50 K and then drops fast to  $1.15 \text{ cm}^3 \text{ mol}^{-1} \text{ K}$  at 2 K. At the highest temperature the magnetic value is higher than the expected spin-only value ( $1.875 \text{ cm}^3 \text{ mol}^{-1} \text{ K}$ ,  $S = 3/2$ ) indicating a high *g* value ( $g > 2.0$ ). The decrease of the  $\chi_M T$  at lower temperatures can be attributed to a combination of two factors: (i) zero-field splitting of the ground state and (ii) intramolecular interactions. Tetrahedral  $\text{Co}^{\text{II}}$  ions ( $S = 3/2$ ) usually show significant zero-field splitting parameters (ZFS), in addition, in this compound the magnetic interaction through the bridging ligand should be negligible ( $J = 0$ ). Therefore, the magnetic behavior has been studied considering only the ZFS effects. This way, the system can be treated by using the following spin Hamiltonian:

$$H = D[S_z^2 - 1/3S(S + 1)] + g_{\parallel} \mu_B H_z S_z + g_{\perp} (H_x S_x + H_y S_y)$$

The final expression used for the fitting of the magnetic susceptibility data was derived from the Hamiltonian above.<sup>21</sup> Fig. 5 shows as a line the least-squares fitting of the experimental data which led to  $|D| = 10.8 \text{ cm}^{-1}$ ,  $g_{\perp} = 1.92$ ,  $g_{\parallel} = 2.92$  and



**Fig. 4** (a) Repeat unit of 1D chain formed by H-bonding among octahedral and tetrahedral cobalt(II) involving uncoordinated water molecules O5 (ball'n'stick) (b) 2D sheet formed *via* H-bonding among parallel H-bonded 1D chains in compound **2**, in the *ab* plane. Cobalt (cyan, ball'n'stick), nitrogen (blue), bromide (green), carbon (grey), and oxygen (red).

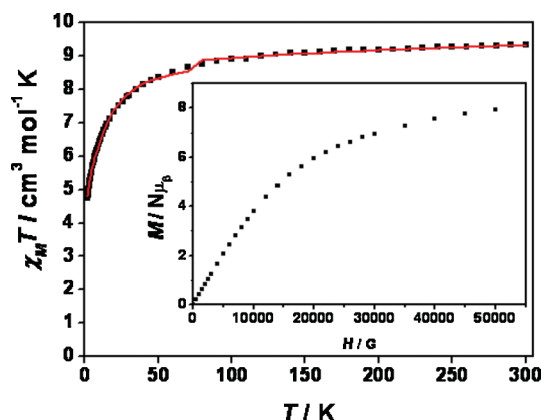


**Fig. 5** Plot of  $\chi_M T$  vs  $T$  and the reduced magnetization  $M/N\mu_B$  vs  $H/T$  (inset) for compound **1**. Squares symbolize the experimental data (inset: applied magnetic fields are added for clarity) and the solid red line the fitting of results.

$TIP = 600 \times 10^{-3} \text{ cm}^3 \text{ mol}^{-1}$  ( $R = 2.8 \cdot 10^{-4}$ ). Similar values of  $D$  and  $g$  have been reported for other tetrahedrally distorted cobalt(II) compounds.<sup>21</sup>

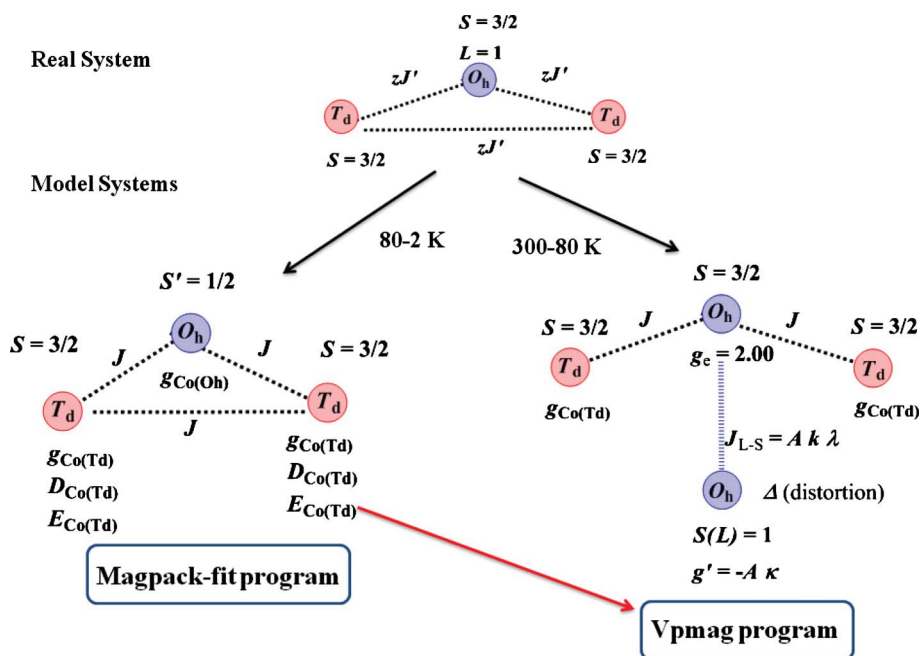
On the other hand, dc magnetization *vs* field measurements were made at applied magnetic fields of 0.5, 1, 2, 3, 4 and 5 T, respectively, in the 1.8–2.5 K range for **1**. Fig. 5 shows the reduced magnetization  $M/N\mu_B$  vs  $H/T$  plots. The data in the figure show that the isofield lines do not overlap, indicating zero-field splitting of the spin ground state. The fitting was performed with a full matrix diagonalization approach.<sup>22</sup> The best results were  $|D| = 11.04 \text{ cm}^{-1}$ ,  $|E| = 0.002 \text{ cm}^{-1}$  and  $g = 2.18$  ( $R = 6.8 \cdot 10^{-4}$ ).

Solid-state, variable-temperature (2.0 K–300.0 K) dc magnetic susceptibility data were collected on polycrystalline samples of compound **2**. The magnetic behavior of this compound is depicted in Fig. 6 as a plot of  $\chi_M T$  vs  $T$ . The  $\chi_M T$  value at room temperature is  $9.32 \text{ cm}^3 \text{ K mol}^{-1}$ . Upon cooling, the magnetic susceptibility data is roughly maintained, exhibiting a plateau that decreases smoothly until 75 K. Below this temperature, it drops faster to a value of  $4.74 \text{ cm}^3 \text{ K mol}^{-1}$  at 1.99 K. On the other hand, magnetization measurements at 2 K and 5 T show a value for the  $M/N\mu_B$  of 7.93 (Fig. 6, inset). The expected  $\chi_M T$  and  $M/N\mu_B$  values for three high-spin  $\text{Co}^{\text{II}}$  ions ( $S = 3/2$  and  $g = 2$ ) under the conditions depicted above should be approximately  $6 \text{ cm}^3 \text{ K mol}^{-1}$  and 9, respectively. The difference between these values and the experimental data may be explained by means of the different geometry around the  $\text{Co}^{\text{II}}$  ions. As has been mentioned before, compound **2** is formed by three  $\text{Co}^{\text{II}}$  ions: a cationic entity,  $[\text{CoL}_2(\text{H}_2\text{O})_4]^{2+}$ , with an octahedral environment and two identical anionic units,  $[\text{CoLBr}_2]^-$ , both exhibiting a tetrahedral environment. The sum of these three  $\text{Co}^{\text{II}}$  species provides a neutral compound and therefore this trinuclear unit was the model used in our magnetic studies. In general, the coordination number and arrangement of the  $\text{Co}^{\text{II}}$  centers have great relevance on the magnetism of the final compounds because such metallic ions will behave differently if their nature is octahedral or tetrahedral. Basically,  $\text{Co}^{\text{II}}$  ions in an octahedral environment ( $\text{Co}_{\text{Oh}}$ ) exhibit spin–orbit coupling, while tetrahedral  $\text{Co}^{\text{II}}$  ions ( $\text{Co}_{\text{Td}}$ ) usually show important zero-field splitting (ZFS) parameters with  $g$  values higher than 2. Also, the  $\chi_M T$  product for a  $\text{Co}_{\text{Oh}}$ , should decrease on cooling, due to the spin–orbit effect, and for  $\text{Co}_{\text{Td}}$  should also decrease due to the ZFS and the experimental data is the superimposition of both graphs.



**Fig. 6**  $\chi_M T$  vs  $T$  and  $M/N\mu_B$  vs  $H$  (inset) plots for compound **2**. Squares symbolize the experimental data and the solid line the fitting of results.

High-spin  $\text{Co}_{\text{Oh}}$  ions exhibit a ground state defined by a term  $^4T_{1g}$  that splits into a sextet, a quartet and a Kramers' doublet



**Scheme 2** Schematic representation of the trinuclear system under study:  $\text{Co}^{\text{II}}_{\text{Td}} \cdots \text{Co}^{\text{II}}_{\text{Oh}} \cdots \text{Co}^{\text{II}}_{\text{Td}}$  and the considered models to fit the experimental magnetic data.

by spin–orbit coupling.<sup>23</sup> At low temperatures, only the Kramers' doublet will be populated and it could be considered as if it would have an effective spin  $S' = 1/2$ . So, the  $M/N\mu_B$  value at 2 K and 5 T should be lower than 9, and  $\sim 7$ , corresponding to two  $S = 3/2$  and one  $S' = 1/2$ , in agreement with the experimental result.

However, in the high temperature range,  $\text{Co}_{\text{Oh}}$  exhibits a ground state of  $S = 3/2$  and the Hamiltonian that describes the spin–orbit coupling for this system is given by the following expression:  $H_{\text{so}} = -A\kappa\lambda LS$ , where  $\lambda$  is the spin–orbit coupling constant,  $\kappa$  is the reduction of the orbital angular momentum caused by the delocalization of the unpaired electrons and  $A$  is a parameter describing the degree of mixing of the two  ${}^4\text{T}_{1g}$  states arising from the ground  ${}^4\text{F}$  and excited  ${}^4\text{P}$  terms of the  $d^7$  free ion. Following the Hamiltonian, if there is an axial distortion in the  $\text{Co}_{\text{Oh}}$ , the triplet orbital  ${}^4\text{T}_{1g}$  ground state would split into a singlet  ${}^4\text{A}_2$  and a doublet  ${}^4\text{E}$  levels with a  $\Delta$  energy gap. The operator responsible for an axial distortion will be expressed as:

$$\Delta \left[ L_z^2 - \frac{1}{3} L(L+1) \right] \quad (1)$$

The full Hamiltonian describing the magnetic properties for an isolated  $\text{Co}^{\text{II}}$  ion, involving the spin–orbit coupling, axial distortion and Zeeman interaction is given by

$$H = -A\kappa\lambda LS + \Delta \left[ L_z^2 - \frac{1}{3} L(L+1) \right] + \mu_B (-A\kappa L + g_e S) H \quad (2)$$

In principle, no analytical expression for the magnetic susceptibility as a function of  $A$ ,  $\kappa$ ,  $\lambda$  and  $\Delta$  can be derived. However, a method to solve this problem has been developed using the program VPMAG, where the values of these parameters can be determined through numerical matrix diagonalization.<sup>24</sup> This program could be a good approach for the study of compound 2, even though the octahedral environment of the  $\text{Co}_{\text{Oh}}$  shows a

rhombic distortion. Therefore, in the following strategy we have considered this fact and applied it as an attempt of determining the parameters that may affect in great manner the experimental data.

Following the discussion above, the experimental magnetic data could be analyzed (and somehow simplified) taking into account two factors: the ZFS parameters of the  $\text{Co}_{\text{Td}}$ , which should lead the shape of the graph in the lower range of temperatures, and the spin–orbit coupling of the  $\text{Co}_{\text{Oh}}$  that should be relevant at the highest. Also, it is important to stress that this compound presents hydrogen bonds between the three mononuclear entities, and antiferromagnetic intermolecular interactions should be considered mostly at the lowest temperatures.<sup>25</sup> Hence, the experimental data were divided in two parts: above and below 80 K, where two independent models were used to obtain the best fit of each section Scheme 2 shows a schematic representation of the real system (top), and the models utilized in this analysis (bottom). The temperature of 80 K was taken as the border line to apply separately the analytical models even though it should not be used as standard.<sup>7</sup> The results of both fittings are represented together with the experimental values in Fig. 6.

Following the Scheme 2, the  $\chi_M T$  vs  $T$  data below 80 K were fitted using the program MAGPACK-fit<sup>26</sup> The spin ground state of  $\text{Co}_{\text{Oh}}$  was considered  $S' = 1/2$ , and the parameters studied were two isotropic  $g$  factors for both types of cobalt(II) ions, respectively ( $g_{\text{Co}_{\text{Td}}}$  and  $g_{\text{Co}_{\text{Oh}}}$ ) and the ZFS parameters of the two  $\text{Co}_{\text{Td}}$  ions ( $D_{\text{Co}_{\text{Td}}}$  and  $E_{\text{Co}_{\text{Td}}}$ ) together with the corresponding exchange coupling parameter between the metallic units.<sup>19</sup> The values obtained from the theoretical correlation at low temperatures are the following:  $g_{\text{Co}_{\text{Td}}} = 2.89$ ,  $g_{\text{Co}_{\text{Oh}}} = 3.50$ ,  $|D_{\text{Co}_{\text{Td}}}| = 10.62 \text{ cm}^{-1}$ ,  $|E_{\text{Co}_{\text{Td}}}| = 2.95 \text{ cm}^{-1}$  and  $J = -0.41 \text{ cm}^{-1}$  ( $R = 4.6 \cdot 10^{-4}$ ). The fitting provides  $g_{\text{Co}_{\text{Td}}}$ ,  $D_{\text{Co}_{\text{Td}}}$  and  $g_{\text{Co}_{\text{Oh}}}$  values which are in the range found for other compounds.<sup>27</sup> The results also improved when weak interactions between the cobalt(II) units were taken into account,

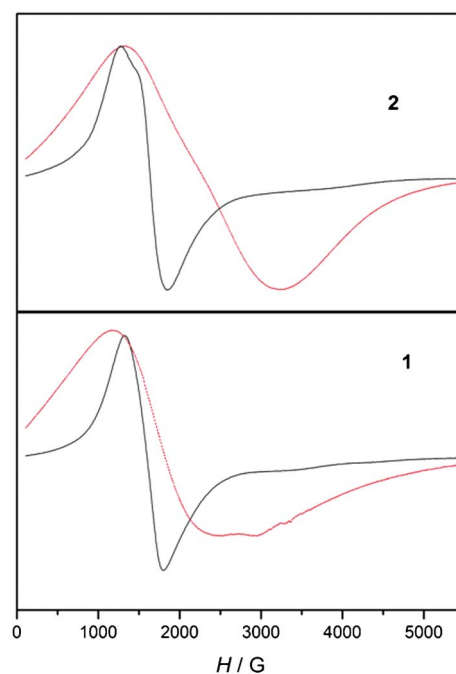
already expected from the crystallographic data.<sup>25</sup> In fact, a recent work from this group in a related trinuclear  $\text{Co}^{\text{II}}_{\text{Td}}\text{-Co}^{\text{II}}_{\text{Oh}}\text{-Co}^{\text{II}}_{\text{Td}}$  compound has shown similar values of those presented in this paper.<sup>7</sup>

On the other hand, the  $\chi_{\text{M}}T$  vs  $T$  data above 80 K was analyzed using the program VPMAG,<sup>24</sup> considering the spin-orbit coupling of the  $\text{Co}_{\text{Oh}}$  and  $g_{\text{CoTd}}$  obtained from the data at low temperatures. The parameters considered in this model are also depicted in Scheme 2. If the spin-orbit coupling parameters are included into the Heisenberg Hamiltonian described in eqn (2), then the first term of this equation would be interpreted as the exchange coupling between two local spin moments, with  $L$  and  $S$  values of 1 and 3/2, respectively and the constant  $J_{L-S}$  will lead this magnetic interaction whose value will be given by  $A\kappa\lambda$ . In a similar way, the second term will represent the zero-field splitting of the triplet  $S(L) = 1$ , due to geometrical distortions. Finally, the Zeeman term would be given in the last term, where two different  $g$ -factors corresponding to the  $S(L) = 1$  and  $S = 3/2$  involved will be taken into account ( $g' = -A\kappa$  and  $g_e = 2.00$ , respectively). Values from the fitting at low temperatures,  $g_{\text{CoTd}}$  and exchange coupling, were taken as fixed in this fitting. In this manner, above 80 K the best fit provided the following parameters:  $A\kappa = 0.74$ ,  $\Delta = 240.9 \text{ cm}^{-1}$  and  $J_{L-S} = -107.1 \text{ cm}^{-1}$  ( $R = 1.9 \cdot 10^{-5}$ ), from where  $\lambda$  was calculated with a final value of  $-144.8 \text{ cm}^{-1}$  ( $J_{L-S} = A\kappa\lambda$ ).<sup>28</sup> The resulting  $A\kappa$  parameter ( $= 0.74$ ) is within this range, indicating weak crystal-field and reasonable covalency due to the nature of ligands, L and  $\text{Br}^-$ , respectively, and to some extent, to their weak interactions with the  $\text{Co}_{\text{Oh}}$  ion. Hence,  $\lambda$  was found to be lower than the free ion value ( $-176 \text{ cm}^{-1}$ ), which is expected after coordination and depends on the covalent character of the M-L bond.<sup>5a,b</sup> These results are similar to other cobalt systems described in the literature.<sup>5c,d,29a,b</sup> Finally, the fitting value obtained for  $\Delta$  indicate distortions from a perfect octahedral  $\text{Co}^{\text{II}}$  geometry and is within the range found in previous works for six-coordinated  $\text{Co}^{\text{II}}$  compounds where  $|\Delta|$  values have been reported between 0 and  $1000 \text{ cm}^{-1}$ .<sup>5</sup>

The values found for the  $\text{Co}_{\text{Td}}$  units in both compounds are very similar. This is important because it reinforces the values obtained for the compound **2** even though one should not forget that approximations had to be taken in the process.

EPR spectra of polycrystalline samples of compounds **1** and **2** were carried out at two temperatures: 77 and 4 K, for **1**, and 50 and 4 K, for **2** (Fig. 7). The spectra at 77 or 50 K showed a broad and asymmetric band with a peak-to-peak  $\Delta H_{\text{p-p}}$  of 1250 G and centered at 1800 G for compound **1** and 1900 G and centered at  $\sim 2280$  G for compound **2**. However, the shape of the band changes drastically on cooling and at 4 K the band is centered at  $\sim 1600$  G for both compounds. At this temperature the spectra of both compounds is similar, but the spectrum of compound **2** shows a shoulder at  $\sim 1500$  G, that is not present in the spectrum of compound **1**. Moreover the band width is significantly larger for **2** than for **1**. ( $\Delta H_{\text{p-p}} = 485$  G for **1** and 560 G, for **2**).

The spectrum of compound **1** corresponds to the  $\text{Co}_{\text{Td}}$ , while for compound **2**, the spectrum at 4 K could be described as the superimposition of the spectra of  $\text{Co}_{\text{Oh}}$  and  $\text{Co}_{\text{Td}}$ . At this temperature, the  $\text{Co}_{\text{Oh}}$ , which exhibits spin-orbit coupling, could be considered as a  $S' = 1/2$  system. On the other hand, the  $\text{Co}_{\text{Td}}$  shows important ZFS parameters and  $g$  values appreciatively different from 2.0. Taking into account these facts, two independent simulations were



**Fig. 7** X-band EPR spectra of crushed crystalline samples of compounds **2** (top) and **1** (bottom) at 50 K (or 77 K for **1**) (dashed red line) and 4 K (solid black line).

carried out using the program Easyspin:<sup>30</sup> (i) for a single  $\text{Co}_{\text{Td}}$  unit, with  $S = 3/2$  with  $D$  and  $E$  and (ii) for one  $\text{Co}_{\text{Oh}}$  with  $S = 1/2$ . The simulation of the former was reasonably attained with the following parameters:  $|D| = 11 \text{ cm}^{-1}$ ,  $|E| = 2.6 \text{ cm}^{-1}$  and  $g \sim 2.8$  values (Fig. 7). For the latter, the simulation of the 1750 G band led to a  $g$  value of 3.8. One should keep in mind that these numbers are approximate and improved simulations may be obtained by means of anisotropic  $g$  values. Nevertheless, it is also relevant to point out that these numbers are in agreement with the values obtained in the magnetic fittings described above.

## Conclusions

In the present work we presented the structural and magnetic properties of the two new  $\text{Co}(\text{II})$  compounds containing  $N,N$ -diisobutylisonicotinamide as the coordinating ligand. This study shows that these fully substituted amide derivatives of pyridine carboxylic acids provide the necessary rigidity and binding sites, thereby enhancing the chances of formation of thermally stable coordination networks (compound **1**) instead of isolated entities. At the same time the increased alkyl bulk on  $N,N$ -diisoalkylisonicotinamides leads to the formation of networks based on mononuclear entities (compound **1**) rather than polynuclear entities.<sup>7</sup> Furthermore, the presence of bulkier and less electronegative bromine atoms in compound **2** leads to the formation of ionic structural units with different geometries in the same compound instead of any coordination network. Finally, intermolecular interactions among 1D coordinated chains (compound **1**) or ionic structural units (compound **2**) made feasible the formation of more compound networks (2D and 3D). Each of these levels contains remarkable features that have been discussed throughout the paper, making both the compounds unique from a structural point of view.



The magnetic behavior of **1** is as expected for isolated tetrahedral Co(II) ions. On the other hand, compound **2** presents intermolecular interactions between the two tetrahedral and octahedral Co(II) ions, which have been estimated from the magnetic data in two separate blocks, above and below 80 K, applying programs VP-MAG and MAGPACK-fit, respectively. Only the most significant effects at each interval of temperature were considered: spin-orbit coupling of the Co( $O_h$ ), at high temperatures and zero-field splitting parameters of the Co( $T_d$ ) at the lowest. Spin-spin magnetic interaction has been taken into account for the whole range of temperatures. Reasonable data for ZFS parameters and spin-orbit parameters have been found to be similar to those reported in the literature. The Co( $T_d$ ) units of compounds **1** and **2** shows similarities in the crystallographic environment and this has been also observed in their magnetic behavior, where ZFS parameters are of the same order. Moreover the EPR spectra are quite similar at low temperatures.

## Acknowledgements

Ajay Pal Singh Pannu thanks UGC-SAP for providing a research fellowship. Dr Pratibha Kapoor thanks CSIR, New Delhi for financial support. Thanks are due to Prof. R. J. Butcher and Prof. M. Martinez-Ripoll for the X-ray data collection of compounds **1** and **2**, respectively. The Spanish authors thank the Ministerio de Educación y Ciencia (CTQ2009-07264/BQU and CTQ2009-06959/BQU), the Comissió Interdepartamental de Recerca i Innovació Tecnològica de la Generalitat de Catalunya (CIRIT) (2009SGR1454) and ICREA (Institució Catalana de Recerca i Estudis Avançats) for financial support.

## References

- (a) *Metal-Organic and Organic Molecular Magnets*, Spec. Publ. –R. Soc. Chem., ed. P. Day and A. E. Underhill, Cambridge, UK, 2000, Vol. 252; (b) K. Itoh and M. Kinoshita, *Molecular Magnetism, New Magnetic Materials*, ed., Gordon Breach-Kodansha, Tokyo, 2000; (c) S. J. Blundell, *Magnetism in Condensed Matter*, Oxford University Press, 2001; (d) C. Janiak, *Dalton Trans.*, 2003, 2781; (e) J. R. Galán-Mascarós and K. R. Dunbar, *Angew. Chem., Int. Ed.*, 2003, **42**, 2289; (f) M. A. Lawandy, X. Huang, Ru-Ji Wang, J. Li, J. Y. Lu, T. Yuen and C. L. Lin, *Inorg. Chem.*, 1999, **38**, 5410; (g) Y. Liu, H. Tsai, Y. Lu, Y. Wen, J. Wang and K. Lu, *Inorg. Chem.*, 2001, **40**, 6426; (h) R. Clerac, F. A. Cotton, K. R. Dunbar, T. Lu, C. A. Murillo and X. Wang, *J. Am. Chem. Soc.*, 2000, **122**, 2272; (i) A. Rujiwatra, C. J. Kepert, J. B. Claridge, M. J. Rosseinsky, H. Kumagai and M. Kurmoo, *J. Am. Chem. Soc.*, 2001, **123**, 10584; (j) S. Midollini, A. Orlandini, P. Rosa and L. Sorace, *Inorg. Chem.*, 2005, **44**, 2060.
- M. Kurmoo, *Chem. Soc. Rev.*, 2009, **38**, 1353.
- J. S. Griffith, *The Theory of Transition-Metal Ions*, Cambridge University Press, 1964.
- A. B. P. Lever, *Inorganic Electronic Spectroscopy*, second Edition, 1984, Elsevier, Amsterdam.
- (a) G. Aromí, H. Stoeckli-Evans, S. J. Teat, J. Cano and J. Ribas, *J. Mater. Chem.*, 2006, **16**, 2635; (b) F. Lloret, M. Julve, J. Cano, R. Ruiz-García and E. Pardo, *Inorg. Chim. Acta*, 2008, **361**, 3432; (c) O. Fabelo, L. Cañadillas-Delgado, J. Pasán, F. S. Delgado, F. Lloret, J. Cano, M. Julve and C. Ruiz-Pérez, *Inorg. Chem.*, 2009, **48**, 11342; (d) M. Fondo, N. Ocampo, A. M. García-Deibe, M. Corbella, M. Salah El Fallah, J. Cano, J. Sanmartín and M. R. Bermejo, *Dalton Trans.*, 2006, 4905.
- M. Yao, M. Zeng, H. Zou, Y. Zhou and H. Liang, *Dalton Trans.*, 2008, 2428.
- P. Kapoor, A. P. S. Pannu, G. Hundal, R. Kapoor, M. Corbella, N. Aliaga-Alcalde and M. S. Hundal, *Dalton Trans.*, 2010, **39**, 7951.
- (a) A. M. Beatty, *CrystEngComm*, 2001, **3**, 243; (b) A. M. Beatty, *Coord. Chem. Rev.*, 2003, **246**, 131.
- (a) C. B. Aakeröy, A. M. Beatty and D. S. Leinen, *Angew. Chem., Int. Ed.*, 1999, **38**, 1815; (b) C. B. Aakeröy and A. M. Beatty, *Chem. Commun.*, 1998, 1067; (c) C. B. Aakeröy, A. M. Beatty and A. Helfrich, *J. Chem. Soc., Dalton Trans.*, 1998, 1943; (d) C. B. Aakeröy, A. M. Beatty, D. S. Leinen and K. R. Lorimer, *Chem. Commun.*, 2000, 935; (e) C. B. Aakeröy and A. M. Beatty, *Cryst. Eng.*, 1998, **1**, 39; (f) C. B. Aakeröy, A. M. Beatty, J. Desper, M. O'Shea and J. Valdes-Martinez, *Dalton Trans.*, 2003, 3956; (g) C. B. Aakeröy, J. Desper and Valdes-Martinez, *CrystEngComm*, 2004, **6**, 413.
- (a) L. Brammer, J. C. Mareque-Rivas, R. Antencia, S. Fang and F. C. Pigge, *J. Chem. Soc., Dalton Trans.*, 2000, 3855; (b) G. Yang, H.-G. Zhu, B.-H. Liang and X.-M. Chen, *J. Chem. Soc., Dalton Trans.*, 2001, 580; (c) J. Emsley, N. M. Reza, H. M. Dawes and M. B. Hursthouse, *J. Chem. Soc., Dalton Trans.*, 1986, 313; (d) Z. Qin, M.-C. Jennings and R. J. Puddephat, *Inorg. Chem.*, 2001, **40**, 6220; (e) M. D. Selby, B. K. Roland, M. D. Carducci and Z. Zheng, *Inorg. Chem.*, 2003, **42**, 1656; (f) C.-H. Chen, J. W. Cai, X. L. Feng, X. M. Chen and J. Chin, *Inorg. Chem.*, 2002, **18**, 659; (g) C. H. Chen, J. W. Cai, C. Z. Liao, X. L. Feng, X. M. Chen and S. W. Ng, *Inorg. Chem.*, 2002, **41**, 4967; (h) V. Zelenak, I. Cisarova and P. Llewellyn, *Inorg. Chem. Commun.*, 2007, **10**, 27.
- A. D. Burrows, C. W. Chan, M. M. Chowdhry, J. E. McGrady and D. M. P. Mingos, *Chem. Soc. Rev.*, 1995, **24**, 329.
- (a) C. H. Chen, J. Cai, X. L. Feng and X. M. Chen, *Polyhedron*, 2002, **21**, 689; (b) J. K. Bera, T.-T. Vo, R. A. Walton and K. R. Dunbar, *Polyhedron*, 2003, **3**, 2009; (c) C. R. Bondy, P. A. Gale and S. J. Loeb, *J. Supramol. Chem.*, 2002, **2**, 93; (d) M. M. Bishop, A. H. W. Lee, L. F. Lindoy, P. Turner, B. W. Skelton and A. H. White, *Supramol. Chem.*, 2005, **17**, 37; (e) V. Zelenak, M. Sabo, W. Massa and P. Llewellyn, *Inorg. Chim. Acta*, 2004, **357**, 2049; (f) J. C. Mareque-Rivas and L. Brammer, *New J. Chem.*, 1998, **22**, 1315.
- (a) I. Ucar, A. Bulut, A. Karadag and C. Kazak, *J. Mol. Struct.*, 2007, **837**, 38; (b) E. Sahin, S. Ide, A. Atac and S. Yurdakul, *J. Mol. Struct.*, 2002, **616**, 253; (c) S. Kahir, I. Bulut and K. Aoki, *J. Chem. Crystallogr.*, 2003, **33**, 875.
- (a) Xiao-Li Zhao and T. C. W. Mak, *Dalton Trans.*, 2004, 3212; (b) M. M. Najafpour, T. Lis and M. Holynska, *Inorg. Chim. Acta*, 2007, **360**, 3452; (c) B. Kozljevcar, I. Leban, I. Turel, P. Segedin, M. Petric, F. Pohleven, A. J. P. White, D. J. Williams and J. Sieler, *Polyhedron*, 1999, **18**, 755.
- (a) J. Moncol, M. Mudra, P. Lönnecke, M. Hewitt, M. Valko, H. Morris, J. Svorec, M. Melnik, M. Mazur and M. Koman, *Inorg. Chim. Acta*, 2007, **360**, 3213; (b) F. Bigoli, A. Braibanti, M. A. Pellinghelli and A. Tiripicchio, *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.*, 1973, **29**, 39.
- (a) B. R. Bhogala, P. K. Thallapally and A. Nangia, *Cryst. Growth Des.*, 2004, **4**, 215; (b) Z. X. Lian, J. Cai, C. Chen and H. Luo, *CrystEngComm*, 2007, **9**, 319; (c) Hong Xu, Yinglin Song and Hongwei Hou, *Inorg. Chim. Acta*, 2004, **357**, 3541.
- (a) P. Kapoor, A. Pathak, R. Kapoor, P. Venugopalan, M. Corbella, M. Rodriguez, J. Robles and A. Llobet, *Inorg. Chem.*, 2002, **41**, 6153; (b) P. Kapoor, A. Kataria, P. Venugopalan, R. Kapoor, M. Corbella, M. Rodriguez, M. Romero and A. Llobet, *Inorg. Chem.*, 2004, **43**, 6699; (c) R. Kapoor, A. Kataria, A. Pathak, P. Venugopalan, G. Hundal and P. Kapoor, *Polyhedron*, 2005, **24**, 1221; (d) R. Kapoor, A. Pathak, P. Kapoor and P. Venugopalan, *Polyhedron*, 2006, **25**, 31; (e) A. P. Swain and S. K. Naegle, *J. Am. Chem. Soc.*, 1957, **79**, 5250.
- (a) A. Altomare, M. C. Burla, M. Camalli, G. Casciarano, C. Giacovazzo, A. Guagliardi, A. G. G. Moliterni, G. Polidori and R. Spagna, *J. Appl. Crystallogr.*, 1999, **32**, 115; (b) G. M. Sheldrick, *SHELX-97: Program for Solution and Refinement of Crystal Structures*, University of Göttingen, Göttingen, Germany, 1997.
- (a) C. Livage, C. Egger and G. Férey, *Chem. Mater.*, 2001, **13**, 410; (b) M. Goodgame and P. J. Hayward, *J. Chem. Soc. (A)*, 1971, 3406; (c) L. Sacconi, I. Bertini and F. Mani, *Inorg. Chem.*, 1967, **6**, 262; (d) J. M. Land, J. A. Stubbs and J. T. Wroblewski, *Inorg. Chem.*, 1977, **16**, 1955; (e) N. Islam, M. R. Islam, S. Ahmad and B. Waris, *J. Am. Chem. Soc.*, 1975, **97**, 3026; (f) P. Day and C. K. Jørgensen, *J. Chem. Soc.*, 1964, 6226; (g) B. D. Bird and P. Day, *J. Chem. Phys.*, 1968, **49**, 392; (h) M. Amiras, A. H. Mahmoudkhani, A. Gorji, S. Dehghanpour and H. R. Bijanzadeh, *Polyhedron*, 2002, **21**, 2733; (i) N. Greenwood, A. Earnshaw, *Chemistry of the Elements*, Pergamon:Oxford, 1984; (j) W. R. Scheidt, J. C. Hanson and P. G. Rasmussen, *Inorg. Chem.*, 1969, **8**, 2398; (k) J. A. Dean, *Section-4 Inorganic Chemistry. Langes Handbook of Chemistry*, McGraw-Hill 1987, p. 4.

- 20 (a) C. L. Schauer, E. Matwey, F. W. Fowler and J. W. Lauher, *J. Am. Chem. Soc.*, 1997, **119**(10), 245; (b) C. L. Schauer, E. Matwey, F. W. Fowler and J. W. Lauher, *Cryst. Eng.*, 1998, **1**, 213.
- 21 D. Kong, Y. Li, X. Ouyang, A. V. Prosvirin, H. Zhao, J. H. Ross, K. R. Dunbar and A. Clearfield, *Chem. Mater.*, 2004, **16**, 3020.
- 22 Software package supplied by E. Rivière, Université Paris Sud (Orsay), France.
- 23 (a) O. Kahn, *Molecular Magnetism*, VCH Publishers, New York, 1993; (b) B. N. Figgis, M. Gerloch, J. Lewis, F. E. Mabbs and G. A. Webb, *J. Chem. Soc. A*, 1968, 2086.
- 24 (a) J. Cano, *VPMAG* package, B.1 revision, University of Valencia, 2003; (b) J. M. Herrera, A. Bleuzen, Y. Dromzée, M. Julve, F. Lloret and M. Verdaguer, *Inorg. Chem.*, 2003, **42**, 7052.
- 25 The program MAGPACK-fit (for the magnetic data between 2 and 70 K) allows the use of the intermolecular interaction parameter,  $zJ'$ ; however, the fitting of the data was performed using a  $J$  parameter (exchange coupling parameter, intramolecular interaction) taken it equal for all the three charged species (the  $\text{Co}(O_h)$  and the two  $\text{Co}(T_d)$ , see Scheme 2). The best fitting was achieved following this procedure although extra calculations using  $zJ$  provided similar values.
- 26 Magpack program: J. J. Borrás-Almenar, J. M. Clemente-Juan, E. Coronado and B. Tsukerblat, *J. Comput. Chem.*, 2003, **9**, 985 Fit: DSTEPIT program. Program 66, Quantum Chemistry Program Exchange, Indiana University, Bloomington, IN.
- 27 (a) L. R. Macgillivray and J. L. Atwood, *J. Chem. Crystallogr.*, 1997, **27**, 453; (b) M. Q. Makinen, L. C. Kuo, M. B. Yijm, G. B. Wells, J. M. Fukuyama and J. E. kim, *J. Am. Chem. Soc.*, 1985, **107**, 5245; (c) A. A. Verberckmoes, B. M. Weckhuysen and R. A. Schoonheydt, *Microporous Mesoporous Mater.*, 1998, **22**, 165; (d) H. R. Jiménez, J. Salgado, J. M. Moratal and I. Morgenstern-Badarau, *Inorg. Chem.*, 1996, **35**, 2737; (e) D. Nelson and L. W. ter Haar, *Inorg. Chem.*, 1993, **32**, 182.
- 28 The limiting value of  $A$  in a weak crystal-field is 1.5, while in strong crystal-fields is equal to 1. On the other hand, the reduction orbital  $\kappa$  fluctuates between 1 and 0.6 depending on covalency, from where it can be extrapolated that the  $A\kappa$  coefficient is always between 0.6 to 1.5.
- 29 (a) Z. Huang, H-B. Song, M. Du, S-T. Chen and X.-H. Bu, *Inorg. Chem.*, 2004, **43**, 931; (b) H. Sakiyama, R. Ito, H. Kumagai, K. Inoue, M. Sakamoto, Y. Nishida and M. Yamasaki, *Eur. J. Inorg. Chem.*, 2001, 2027.
- 30 Easy Spin, a comprehensive software package for spectral simulation and analysis in EPR. S. Still and A. Schweiger, *J. Magn. Reson.*, 2006, **178**, 42–55.